

"On the Measurement of the Pressure Coefficient of Oxygen, at Constant Volume, and different Initial Pressures." By WALTER MAKOWER, B.Sc., and HENRY R. NOBLE, B.Sc. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received June 26, 1903.

The Pressure Coefficient of Oxygen.

1. *Introduction.*—Travers and Jaquerod have recently carried out a series of measurements of the pressure coefficients of hydrogen and helium, and, in conjunction with Senter, have applied their results to the measurement of the vapour pressures of liquid oxygen and liquid hydrogen on the constant volume helium and hydrogen scales.* At the conclusion of this research Dr. Travers suggested that we should make an attempt to determine the pressure coefficient of oxygen, which seemed to present those peculiar difficulties which are always associated with measurements involving the observation of mercury surfaces in contact with this gas. The apparatus employed has been previously described by Travers and Jaquerod.†

2. *Previous Determinations.*—Regnault attempted to measure the pressure-coefficient of oxygen, but failed to obtain concordant results. He attributed his failure to the oxidation of the mercury in the manometer used to measure the pressure of the oxygen.‡

Von Jolly§ obtained the value 0.0036743 as the mean of eighteen observations at an initial pressure of about 760 mm. The individual observations are, however, very discordant, varying between 0.003680 and 0.003668.

3. *Preparation of the Oxygen and its Introduction into the Thermometer.*—The oxygen used was prepared by heating pure dry potassium permanganate. The oxygen so generated was passed over soda-lime and liquefied by passing it into a glass spiral immersed in liquid air. By lowering the vessel containing the liquid air, the oxygen could be allowed to boil off gently. In this way any trace of water vapour or other impurity which might have been present was completely removed.

The method of introducing the gas into the thermometer was precisely the same as that employed by Travers and Jaquerod.||

The thermometer bulb, which at the beginning of the research contained helium, was exhausted to a high vacuum, along with the apparatus employed for generating the oxygen. The thermometer was then filled with pure oxygen and after a short time again exhausted.

* 'Phil. Trans.,' A, vol. 200, p. 105.

† *Loc. cit.*

‡ 'Pogg. Ann.,' vol. 55, p. 391, 1842.

§ 'Pogg. Ann.,' Jubelband, p. 82, 1874.

|| *Loc. cit.*

This was repeated a second time, care being taken to admit just the quantity required to fill the apparatus to the pressure desired for taking observations. The instrument was then ready for use.

4. *Correction of Pressure Measurements for Parallax.*—The pressures exerted by the oxygen in the thermometer bulb were determined by measuring the height of a mercury column on a glass scale placed in front of it. In these circumstances errors due to parallax were apt to occur in the observations, unless great care was taken to bring the axis of the telescope into line with the top of the meniscus, or the glass point. This means that all readings were to be made at the intersection of the cross wires in the telescope. It was obviously impossible to read both point and meniscus at the centre simultaneously. A series of observations was therefore taken to determine in what way the apparent distance between a fixed graduation on the scale and the glass point (which was, of course, also fixed) varied with the position of the axis of the telescope. Care was always taken to adjust the telescope so as to make the parallax correction small and in most cases negligible; but when necessary the appropriate correction was applied.

5. *Calculation of Results.*—The pressure of the oxygen contained in the thermometer bulb was measured at the freezing point and at the boiling point of water.

The pressure coefficient (α) was deduced from the well-known definition

$$\alpha = \frac{P_\theta - P_0}{P_0 \theta},$$

where P_θ is the pressure at the boiling point (θ) of steam on the Centigrade scale

and P_0 that at the freezing point at a constant volume unity;

P_θ and P_0 were calculated respectively from the formulæ

$$P_0 = P \left(V_b + \frac{273v_s}{273+t_s} + \frac{273v}{273+t} \right)$$

$$P = P' \left(V_b' + \frac{\theta v_s'}{273+t_s'} + \frac{\theta v'}{273+t'} \right)$$

where P is the observed pressure at the ice point

and P' is that at the steam point,

t_s and t_s' are the temperatures Centigrade at the ice and steam point observations respectively,

t and t' are the temperatures of the dead space at the ice and steam point observations,

V_b is the volume of the bulb at the ice point 94.2096 c.c.,

V_b' is the volume of the bulb at the steam point 94.2096 (1 + 0.0000285 θ),

v_s is the volume of the stem (1.031 c.c.),

v is the volume of the dead space.

Correcting to a constant volume unity simplifies the calculation.

The volume of the dead space from a mark on the stem to a mercury meniscus of height 0.125 cm. in contact with the glass point was 0.3904 c.c.

To obtain the total volume of the dead space it is necessary to apply a correction to allow for the fact that the mercury meniscus was not brought exactly into contact with the glass point. This correction amounts to $\pi r^2 \Delta$, where Δ is the distance between the surface of the mercury and the point and r is the radius of the tube (0.45 cm.). As the height of the mercury meniscus was found to vary considerably in the various experiments, it was necessary to introduce a further correction to allow for the variation of the volume of the dead space from this cause. Assuming the curvature of the meniscus to be constant, the correction to be added is $\frac{1}{2}\pi r^2 (h' - h) - \frac{1}{6}\pi (h'^3 - h^3)$, where h is the height at which the meniscus stood when the volume of the dead space was measured and h' is the height in the particular experiment.

6. *Method of Observation and Results.*—The measurements of pressure were taken in the manner adopted by Travers and Jaquero.* Readings of the ice point and steam point were taken in most instances in alternate pairs, one series of observations being taken by each of us for each setting.

To illustrate the order of accuracy obtained, one series of observations is given in full, in the accompanying table. In the other series only the final corrected values are given.

Details of Series III.

Ice Point.

Observed pressure in millimetres corrected.	Volume of dead space in c.c.	Temperature centigrade of dead space.	Temperature centigrade of stem.	P ₀ .	Mean P ₀ .
707.77	0.4087	14.4	16.5	670.223	670.200
707.76	0.4076	14.4	16.2	670.213	
707.83	0.3919	14.5	15.9	670.166	
707.88	0.3926	14.4	16.7	670.228	
707.71	0.4132	14.4	17.3	670.194	
707.75	0.4132	14.4	17.4	670.232	
707.83	0.3932	14.5	15.7	670.182	
707.84	0.3929	14.4	15.3	670.190	
707.75	0.4105	14.5	16.9	670.218	
707.73	0.4104	14.4	16.2	670.199	
707.79	0.4009	14.5	18.0	670.192	
707.78	0.3983	14.6	17.4	670.161	

* *Loc. cit.*

Steam Point.

Observed pressure in millimetres corrected.	Volume of dead space in c.c.	Temperature centigrade of dead space.	Temperature centigrade of stem.	Barometric pressure.	Temperature centigrade of steam.	P _a .	P _θ - P ₀ (mean).	$\frac{P_{\theta} - P_0 \text{ (mean)}}{\theta}$
964.52	0.4004	14.4	22.7	772.1	100.447	917.519	247.319	2.46218
964.53	0.4000	14.4	21.1	772.0	100.444	917.548	247.348	2.46255
964.53	0.3938	14.5	22.0	771.5	100.425	917.461	247.261	2.46215
964.54	0.3950	14.5	23.2	771.2	100.415	917.480	247.280	2.46238
964.16	0.4199	14.4	22.4	770.6	100.392	917.437	247.237	2.46272
964.14	0.4240	14.5	23.2	770.8	100.400	917.466	247.266	2.46281
964.36	0.4064	14.5	22.5	770.6	100.392	917.444	247.244	2.46279
964.38	0.4053	14.5	23.0	770.8	100.400	917.453	247.253	2.46268
964.27	0.4164	14.5	22.3	771.1	100.410	917.484	247.284	2.46274
964.28	0.4149	14.6	21.7	771.2	100.415	917.493	247.293	2.46271
964.38	0.3999	14.6	21.4	770.5	100.388	917.405	247.205	2.46250
964.37	0.4019	14.5	20.0	770.5	100.388	917.415	247.215	2.46260

$$\text{Mean } \frac{P_{\theta} - P_0 \text{ (mean)}}{\theta} = 2.46258.$$

$$\text{Mean coefficient} = 0.00367440.$$

Final Results.

Number of series.	Ice point.			Steam point.		Coefficient.
	Initial pressure in millimetres of mercury.	Number of observations.	Mean P_0 .	Number of observations.	Mean $\frac{P_\theta - P_0}{\theta}$	
I	698.3	12	661.248	28	2.42848	0.0036726
II	378.6	12	358.444	12	1.3154	0.0036697
III	707.8	12	670.200	12	2.46258	0.0036744
IV	369.1	10	349.538	10	1.2828	0.0036700
V	695.6	2	658.685	2	2.42039	0.0036745

Five series of observations were taken, which are indicated in the first column of the table by Roman figures. The pressure of the gas, when the bulb was in ice, is tabulated in the second column. In the third and fifth columns the number of individual observations are recorded. The final corrected values of P_0 and $\frac{P - P_0}{\theta}$ are inserted in the fourth and sixth columns respectively.

After Series I had been taken, about half of the oxygen contained in the bulb was allowed to escape, and the second series obtained. The thermometer bulb was then completely evacuated and refilled with fresh oxygen, which was used in Series III and IV. The thermometer was again evacuated and refilled with fresh oxygen, with a view to taking another set of observations; but owing to an unfortunate accident to the apparatus, the work was interrupted after the two observations recorded in Series V had been obtained.

On plotting the values of the coefficient against the initial pressures, the value at zero initial pressure is found on linear extrapolation to lie between 0.003664 and 0.003665, a value which is higher than that similarly obtained for nitrogen from Chappuis's determinations, and likewise higher than the pressure coefficient of hydrogen, 0.0036625, obtained by Travers and Jaquero. The difference, although possibly within the limits of experimental error, might be explained on some such assumption as the association of the gas molecule at lower temperatures.

Calculation of the Thermodynamical Correction at Zero Temperature from the Pressure Coefficient and known Data.

It is of interest to deduce the scale correction at 0° C for oxygen, using the method suggested by Callendar,* and the coefficient calculated above. The notation adopted is as follows:—

* 'Phil. Mag.,' vol. 25, 1903, p. 48.

E = intrinsic energy of fluid per unit mass.

p = pressure ; v = volume of unit mass.

$F = E + pv$ = total heat of fluid per unit mass.

H = heat supplied per unit mass from external sources.

$Q = (d\theta/dp)_F$ = "cooling effect" or fall of temperature per unit fall of pressure in adiabothermal expansion at constant F .

$S = (dH/d\theta)_p$ = specific heat of fluid at constant pressure.

$T = (pv/R)$ = temperature by gas thermometer.

θ = temperature on thermodynamic scale.

At the point in the neighbourhood of 50° C. , the degrees on the scale of the gas thermometer are of the same size as those on the absolute scale, $dT/d\theta = 1$, and as is shown in the paper quoted above, the difference between the temperature on the gas scale and on the absolute scale is given approximately by the formula

$$\theta - T = Sp \frac{Q}{R} + \left(\frac{d(pv)}{dp} \right)_\theta \frac{p}{R} \dots\dots\dots (1).$$

The term $(d(pv)/dp)_\theta$ can be evaluated, as shown by Callendar, in the following manner :—Assuming the characteristic equation of the gas to be

$$v = \frac{R\theta}{p} - c + b \dots\dots\dots (2),$$

where

$$c = \frac{a}{R\theta^2} = c_0 \left(\frac{\theta_0}{\theta} \right)^n \dots\dots\dots (3),$$

it may be shown that

$$SQ = (n+1) c - b \dots\dots\dots (4),$$

and that

$$d(pv)/dp = -(c-b) \dots\dots\dots (5).$$

The index n depends on the nature of the gas, and may be taken as 1.5 for oxygen.

From the Joule-Thomson results,* we have for oxygen at 92° C. , $SQ = 1.41 \text{ c.e.}$, and at 8.7° C. , $SQ = 2.88 \text{ c.e.}$; S being expressed in units of 10^6 ergs.

Hence from equations (3) and (4),

$$c_0 = 1.92 \text{ c.e. and } b = 1.70 \text{ c.e.}$$

At 50° C. ,

$$c = 1.49,$$

substituting in equation (5)

$$d(pv)/dp \text{ at } 50^\circ \text{ C.} = -(1.49 - 1.70) = +0.21 \text{ c.e.}$$

* Joule's Collected Papers, vol. 2, p. 348.

Taking $SQ = 1.98$ c.c. at 50°C. , which is obtained by interpolating between 0° and 100°C. , on the assumption that the cooling effect varies inversely as the square of the absolute temperature, and taking the mean of the results so obtained; taking $R = 2.59 \times 10^6$, and p (the pressure at 50°C.) = 81 cm. mercury = 1.08×10^6 (CGS), we have from equation (1) $\theta - T = 0.913$. Hence since the scale correction at 50°C. may be neglected in comparison with the zero correction, $\theta_0 - T_0 = 0.913$.

Now the pressure coefficient, as determined above, at an initial pressure of 70 cm. of mercury is 0.003674, whence

$$T_0 = \frac{1}{0.003674} = 272.18.$$

θ_0 is thus equal to 273.09 , a result which is in good agreement with the value of the same quantity obtained by Callendar* for air, nitrogen, and hydrogen.

It will be observed by reference to equation (5) that $d(pv)/dp$ changes sign at a temperature 23°C. , at the pressure employed in the above experiments.

In conclusion we desire to express our very best thanks to Dr. Travers, not only for his kindness in putting his apparatus at our disposal, but also for the unfailing interest which he has shown in the progress of the work.

* *Loc. cit.*